

(12) UK Patent Application (19) GB (11) 2 342 349 (13) A

(43) Date of A Publication 12.04.2000

(21) Application No 9923941.0

(22) Date of Filing 08.10.1999

(30) Priority Data

(31) 9821980

(32) 08.10.1998

(33) GB

(71) Applicant(s)

Richard Dudley Shaw

Dunedin, High Elms Road, Downe, ORPINGTON, Kent,
BR6 7JN, United Kingdom

(72) Inventor(s)

Richard Dudley Shaw

(74) Agent and/or Address for Service

fJ Cleveland

40-43 Chancery Lane, LONDON, WC2A 1JQ,
United Kingdom

(51) INT CL⁷

C04B 35/63

(52) UK CL (Edition R)

C1J JRB J111 J113 J121 J124 J135 J139 J140 J206
J209

(56) Documents Cited

EP 0824092 A1

US 4769074 A

(58) Field of Search

UK CL (Edition R) C1J JPA JRB

INT CL⁷ C04B 35/63

ONLINE: EPODOC, JAPIO, WPI

(54) Abstract Title

Binding refractories

(57) A method of making a cast refractory comprises providing an aqueous silica sol binder having a pH of about 10.1 to 10.6, preferably about 10.2; mixing the silica sol binder with a refractory aggregate to form a mobile slurry; introducing the slurry into a mould; allowing the slurry to gel to form a green shape; and thereafter stripping the mould from the shape; wherein small amounts of phosphate and magnesium oxide are mixed with the binder to provide rapid and controllable gelling of the slurry and rapid setting of the shape.

The magnesium oxide may be in the form of magnesia, magnesium hydroxide, or magnesium alumina spinel.

GB 2 342 349 A

IMPROVEMENTS IN OR RELATING TO CAST REFRACTORIES

The present invention relates to cast refractories, and has particular reference to
5 an improved method of binding such refractories to form a green shape prior to firing.

Cast refractories that have a precise moulded shape and are dimensionally stable
are required for a number of industrial applications. For instance, such refractories
10 are used as glass feederware in the manufacture of glass objects such, for example, as bottles. They are also used as moulds in the manufacture of metal castings having complex or intricate shapes and as control nozzles for molten steel in continuous casting.

15 In making such refractory castings, the refractory material is mixed with a liquid binder, and the resulting slurry is then added to a mould having the desired shape. This may be done by vibration casting or as a mobile slip, or by a combination of the two. In the mould, the mixture of refractory and binder is allowed to set to form a green shape, in which the refractory material is held together by the
20 binder. The mould is then stripped away, and the green shape is commonly fired in a kiln. During the process of firing, the bonds formed by the liquid binder are

generally weakened and broken, and they are replaced during sintering with oxide bonds between refractory grains. When making high precision, dimensionally stable refractory castings, it is important to ensure that gelling of the refractory/binder mix takes place in a controlled fashion. It is also desirable for
5 the gelling and subsequent hardening to occur rapidly, as this allows a satisfactory manufacturing through-put of product.

The Shaw and Zirconal processes have historically provided convenient and effective ways of setting refractory aggregates to form green shapes for use in the
10 manufacture of precision refractories and precision moulds for metal casting. However, both of these processes involve the use of an alkoxide, particularly ethyl silicate, as the binder. Whilst ethyl silicate is an excellent binder, which gives a high degree of dimensional stability, the use of ethyl silicate as such is undesirable, because it leads to the evolution of ethanol, which represents a health
15 hazard in the work place. Additionally other undesirable hydrocarbons are frequently generated, for example amines.

More recently aqueous silica sol, which is a moderately stable, mildly alkaline dispersion of silica particles in water, has been used in place of ethyl silicate as
20 a binder for binding various refractories. Silica sol, however, suffers from the disadvantage that when used as a binder it takes a long time after initial gelling

to form a strong green shape. Attempts have therefore been made to speed up the gelling and setting of silica sol in a controllable way.

EP-A-0824092 (Shaw) discloses an improved refractory binder based on silica sol
5 which comprises a cogel of phosphate with silica sol and a small amount of
magnesia or magnesium hydroxide. In use, the phosphate gels and hardens more
quickly than the sol to provide a green shape having sufficient strength and
stability to allow the mould to be stripped before the sol has set fully. By
adjusting the amount of magnesia/magnesium hydroxide, the refractory binder of
10 EP-A-0824092 has a controllable gelling time and can, if desired, be used to
provide surprisingly rapid gelling and setting times. The refractory binder of EP-
A-0824092 does have a number of drawbacks however, particularly the use of
fairly high proportions of phosphate. The preferred phosphate is polyammonium
phosphate, but this has the disadvantage that it leads to the evolution of gaseous
15 ammonia which is undesirable from a health and safety perspective. Alkaline
phosphates based on sodium or potassium are also undesirable, because they form
low melting point impurities in the resultant refractory objects.

US-A-3804650 (Meissner et al.) discloses a method of binding refractory materials
20 to form green shapes comprising mixing said refractory materials with an aqueous
silicate solution, such as silica sol, having a pH of about 10-15, and a gelation

agent comprising magnesium oxide and/or an organic compound, such as formaldehyde, methyl formate or the like. It has been found however, that the use of magnesium oxide alone as a gelation agent makes it difficult to control the gelling time of a silica sol binder, and, as disclosed by Meissner et al., an
5 additional organic accelerator is required to shorten the post-gelling setting time.

An object of the present invention is to provide an improved method of making a cast refractory.

10 In particular, an object of the present invention is to provide an improved method of binding refractory materials to form green shapes prior to firing.

Another object of the present invention is to provide a method of binding refractory materials using colloidal silica which is controllable, and can be
15 adjusted to provide rapid gelling and hardening times, but does not require the addition of large amounts of phosphate or other impurities.

Yet another object of the present invention is to provide an improved method of binding refractory materials which is acceptable from the health and safety point
20 of view, and in particular does not involve the use of ammonia or organic compounds.

According to one aspect of the present invention therefore there is provided a method of making a cast refractory; said method comprising providing an aqueous silica sol binder having a pH of about 10.1 to 10.6; mixing the silica sol binder with a refractory aggregate to form a mobile slurry; introducing the slurry into a mould; allowing the slurry to gel to form a green shape; and thereafter stripping the mould from the shape; wherein small amounts of phosphate and magnesium oxide are mixed with the binder to provide rapid and controllable gelling of the slurry and rapid setting of the shape.

10 Silica sol is generally stable at a pH of about 9.4. Thus, commercially available silica sol is generally supplied at about pH 9.4. If the pH of silica sol is reduced below about 9, or is increased above about 10.6, then the silica sol becomes unstable and begins to gel in an uncontrolled fashion. For example, a mixture of silica sol and polyammonium phosphate, which is substantially neutral, sets over
15 a period of 24 hours or so. It has been found however that if the pH of silica sol is increased in a carefully controlled manner to about 10.1-10.6, then a relatively stable sol can be produced. Surprisingly it has further been discovered that a silica sol having a pH in this range can be caused to gel rapidly and controllably by the addition of a small amount of magnesium oxide in the presence of a small
20 amount of phosphate to form a very satisfactory uniform gel, and the resultant gel then sets rapidly to form a shape which can be fired if desired.

By 'magnesium oxide' herein is meant any inorganic compound or compounds comprising an active oxide of magnesium, including magnesia and magnesium hydroxide, as well as mixed oxides of magnesium and other metals, such, for example, as magnesium spinels and magnesium oxide that is fused or sintered with other relatively inert, common refractory oxides such as Al_2O_3 , Cr_2O_3 and ZrO_2 . The activity of the magnesium oxide can be controlled by adjusting the particle size of the magnesium oxide by sintering or fusing, e.g. by calcining. Alternatively, less reactive forms of magnesium oxide, such as magnesium aluminium spinel may be used.

10

Typically a sufficient quantity of magnesium oxide is added to the silica sol binder to raise the pH and initiate controlled gelling of the silica sol. In contrast, it has been found that if silica sol having a pH of about 9.4 is mixed with a gelling agent to increase the pH of the sol for gelling, then although the gel forms rapidly, the overall quality of the gel is poor in comparison.

15

The amount of magnesium oxide added to the sol may be 0.01 to 25%wt, based on the total weight of the refractory aggregate. It is preferred to use as little magnesium oxide as possible to achieve controlled gelling and setting, and thus preferably 0.05-5%wt, and more preferably less than 2.5%wt, magnesium oxide is used. The actual amount of magnesium oxide added in any given case will of

20

course depend upon the form (activity) of magnesium oxide used and the desired setting time. In some examples, 0.25%wt, 0.5%wt, 0.75%wt, 1.0%wt, 1.25%wt or 1.5%wt magnesia or magnesium hydroxide may be used. Where magnesia is used, for example, 0.1-5%wt calcined magnesia may be added to the sol. Magnesium alumina spinel is a preferred magnesium oxide, and the amount of spinel used may be varied over a wide range of addition, thus providing convenient control of setting time. As the proportion of magnesia in the spinel increases, the speedier the reaction. The addition can be as little as 0.5% with a 50% magnesia spinel, or as much as 50%wt of the body with a 75% magnesia spinel.

10

The magnesium oxide may be added to the sol before mixing with the aggregate. Said magnesium oxide may be added to the sol as a dispersion in water, or as a powder. Alternatively, said magnesium oxide may be added in powder form to the refractory material, prior to mixing with the sol, as convenient.

15

It has been unexpectedly found that the addition of a small proportion of phosphate to a silica sol binder, having an elevated pH, provides a greater degree of control over the gelling, and more rapid setting, of the silica sol in the presence of magnesium oxide. Said phosphate may comprise one or more phosphate compounds. Suitable phosphates include, for example, sodium phosphates, such as sodium monophosphate (supplied by Clinochem as "P61"), potassium

20

phosphates, such as monopotassium phosphate (supplied by Clinochem as "P71") and tetrapotassium pyrophosphate, and ammonium phosphates, such as monoammonium phosphate (supplied by Clinochem as "P81").

5 The amount of phosphate to be added to the binder will depend on the actual phosphate used in any given case, and on the desired gelling and setting times. Preferably as little phosphate as possible is employed, so as to minimise the amount of impurities in the eventual casting. It is thought that rather than forming an effective cogel with the sol, the phosphate may act to buffer the pH of the sol
10 in the presence of magnesium oxide and refractory grogg, thus providing greater control over the gelling time. Typically however, about 0.01-25%wt phosphate, based on the total weight of the refractory grogg, is used, preferably 0.01-5%wt, and more preferably 0.01-1.0%wt, e.g. 0.05%wt, 0.1%wt, 0.25%wt, 0.5%wt or 0.75%wt. The amount of phosphate added to the silica sol may be in the range
15 0.5% to 2.5% weight based on the sol.

In some embodiments, said phosphate may have a pH in the same range as the sol. Thus, said phosphate may have a pH of about 10.1 to 10.6. Tetrapotassium pyrophosphate, having a pH of about 10.2, is especially preferred. Whilst those
20 skilled in the art may expect the addition of such phosphate to act as a buffer on the silica sol, it has surprisingly been found that the addition of phosphate to sol

at this pH causes a reduction in pH to about 8 and initiates setting of the slurry:

The phosphate may be added to the sol before mixing with the grog. Said phosphate may be added to the sol as a solution in water, or as a powder and dissolved in the sol. Alternatively, said phosphate may be added in powder form to the refractory material, prior to mixing with the sol, as convenient. In one embodiment, a 25% by weight solution of tetrapotassium pyrophosphate may be used. A remarkably small addition of this solution will cause controlled gelling of the silica sol. A firmer gel may be generated by using sol at a pH of 10.2.

10

Said phosphate and magnesium oxide may be added to the sol or aggregate simultaneously, optionally as a pre-prepared mixture, or sequentially. Said mixture may, for instance, comprise 0.25%-3%wt monosodium phosphate or monopotassium phosphate and an equivalent amount of magnesia or magnesium hydroxide, based on the total weight of aggregate.

15

The pH of the sol may be raised from about 9.4 to pH 10.1 to 10.6 by the addition of any suitable basic reagent. In some embodiments said basic reagent may be selected from one or more of ammonium hydroxide, potassium hydroxide, sodium hydroxide, sodium silicate, sodium aluminate and potassium silicate. The amount of basic reagent added will depend on the actual reagent used in any given

20

case, and will be sufficient to raise the pH of the sol to pH 10.1 to 10.6.

The pH of the silica sol may be elevated to pH 10.1-10.5; preferably pH 10.1 to 10.3, and more preferably 10.15-10.25. In some embodiments, the sol may have
5 a pH of about 10.2.

Said silica sol may have a solids content in the range 15 to 50% by weight. The actual solids content in any given case will depend upon the final refractory applications to a large extent. Said sol may consist of particles of silica having
10 a diameter of 5 to 20nm. The viscosity of the sol may be in the range 1 to 20cp, preferably 8 to 15cp. The specific gravity of the sol may be in the range 1.1 to 1.5.

Said refractory aggregate may consist of grains of any suitable refractory material
15 that is known in the art for making high precision refractory objects or shapes, including moulds. In particular, the refractory aggregate may comprise one or more of zircon, zirconia mullite, alumina, alumina silicates, spinel, silicon carbide or silica, although it is envisaged that the invention can be practised without undue difficulty with any suitable refractory aggregate material, with the exception of
20 very basic refractories such as magnesite or dolomite.

In another aspect of the present invention there is provided a refractory object that is produced in accordance with the method of the present invention. Said object may be an item of glass feederware such, for example, as a plunger or orifice ring for use in the manufacture of glass bottles, or sagger box to fire ceramic ware to high temperatures. The object may comprise a mould for making a ferrous or a non-ferrous casting, as typically made for Shaw Process, Unicast process or the like.

Following is a description by way of example only of embodiments of the present invention.

Description 1

An aqueous silica sol of 30% wt SiO_2 having a pH of 9.4 is provided. The sol is elevated in pH to pH 10.2 by the slow, careful addition of potassium silicate - for example Crossfield Grade 66 - while stirring vigorously. The pH is measured with a suitable pH meter. This solution is useable for significant time without noticeable deterioration - say two to three months.

Example 1

54kgs of a sillimanite refractory aggregate were provided. To this refractory aggregate were added 135g (0.25% wt) of a 50/50 monosodium phosphate/dipotassium phosphate mix in powder form, and 540g (1% wt) of Lycal MgO 93/12 in powder form. To this mixture was added 5400mls (100mls/kg) of the silica sol 30 at pH 10.2 of Description 1 which was sufficient to wet properly the grains and to make a castable slurry when vibrated.

10 The slurry was mixed quickly and thoroughly, and poured into a mould. The slurry took about 40 minutes to gel, and was strong enough to demould after 1 hour.

Example 2

15

54kgs of a sillimanite refractory aggregate were provided. To this refractory aggregate were added 540g (1% wt) of a 50/50 monosodium phosphate/dipotassium phosphate mix in powder form; 1850g (2% wt) of MgO Tanbase (325 mesh calcined MgO) in powder form; and 100g (0.2% wt) of Lycal MgO 93/12 in powder form. 5400mls (100mls/kg) of a silica sol 30 at pH 10.2, prepared as per Description 1 were added, to form a slurry.

The slurry was mixed quickly and thoroughly, and poured into a mould. The slurry took about 15 minutes to gel, and was strong enough to demould after 25 minutes.

5 **Example 3**

54kgs of a sillimanite refractory aggregate were provided. To the refractory aggregate were added 108g (0.2% wt) of Lycal 93 and 27g (0.05% wt) of MgO 96, each in powder form. The resulting aggregate mix was split into three batches of 18kg each. Each batch was mixed with 1800mls (100mls/kg) of Clinosol 3105 silica sol binder at pH10.2 containing 0.15%wt powdered monosodium phosphate (pH 4.5), to form a slurry. Clinosol 3105 silica sol includes 30% silica at a 10 μ particle size.

15 The slurry was mixed quickly and thoroughly, and poured into a mould. The slurry took about 35 minutes to gel, and was strong enough to demould after 50 minutes.

Example 4

20

Example 3 was repeated except the amount of MgO 96 added to the refractory

aggregate was increased to 81g (0.15%). The final aggregate/sol slurry took about 4 minutes to gel, and was strong enough to demould after about 10 minutes.

The green shape produced according to any of the above examples must be
5 allowed to dry after removal from the mould drying will further harden the gel as water is removed. Although traditionally fired thereafter to create a sintered bond - for example by firing the resultant piece to 1400°C - the ceramic piece might well be strong enough in its final application at a lower temperature. Indeed, in some embodiments no firing may be necessary; only drying out at between 200-
10 300°C.

Clearly any of the above examples could be carried out using either a lower silica content or high silica content silica sol. This would be a function of the application. Those skilled in the art of refractory manufacture will readily
15 recognise when and if a higher or lower concentration is required. This would not be outside the generality of the description of this invention, whose purpose is to provide a sufficiently strong gel for the application required.

It should be noted that a further advantage of the sol at pH 10.1-10.6 is that it
20 avoids localised gelling, and avoids premature gelling with many refractory materials including zircon from some sources and certain grades of fine reactive

aluminas: Premature or anti-gelling means an uncontrolled or unpredictable gel, an undesirable feature in any ceramic moulding process.

CLAIMS

1 A method of making a cast refractory; said method comprising providing
an aqueous silica sol binder having a pH of about 10.1 to 10.6; mixing the silica
5 sol binder with a refractory aggregate to form a mobile slurry; introducing the
slurry into a mould; allowing the slurry to gel to form a green shape; and
thereafter stripping the mould from the shape; wherein small amounts of phosphate
and magnesium oxide are mixed with the binder to provide rapid and controllable
gelling of the slurry and rapid setting of the shape.

10

2 A method as claimed in claim 1, wherein the pH of said sol is in the range
10.15 - 10.25.

15

3 A method as claimed in claim 1 or claim 2, wherein said magnesium oxide
comprises magnesia or magnesium hydroxide.

4 A method as claimed in claim 1, claim 2 or claim 3, wherein said
magnesium oxide comprises sintered, fused or calcined magnesia.

20

5 A method as claimed in claim 1 or claim 2, wherein said magnesium oxide
comprise magnesium alumina spinel.

6 A method as claimed in any preceding claim, wherein the amount of magnesium oxide added to the sol is 0.01 to 25%wt, based on the total weight of the refractory aggregate.

5 7 A method as claimed in any preceding claim, wherein the amount of magnesium oxide added to the sol is 0.01 to 5%wt, based on the total weight of the refractory aggregate.

8 A method as claimed in any preceding claim, wherein the magnesium
10 oxide is added to the sol before mixing with the aggregate.

9 A method as claimed in any of claims 1-7, wherein said magnesium oxide is added in powder form to the refractory material, prior to mixing with the sol.

15 10 A method as claimed in any preceding claim, wherein said phosphate is selected from one or more of: sodium phosphates, such as sodium monophosphate; potassium phosphates, such as tetrapotassium pyrophosphate and monopotassium phosphate; and ammonium phosphates, such as monoammonium phosphate.

20 11 A method as claimed in any preceding claim, wherein the amount of phosphate mixed with the binder is 0.01-25%wt phosphate, based on the total

weight of the refractory grogg.

12 A method as claimed in any preceding claim, wherein the amount of
phosphate mixed with the binder is 0.01-5%wt phosphate, based on the total
5 weight of the refractory grogg.

13 A method as claimed in any preceding claim, wherein said phosphate
comprises a phosphate having a pH in the range 10.1-10.6.

10 14 A method as claimed in claim 13, wherein said phosphate comprises
tetrapotassium pyrophosphate.

15 A method as claimed in any preceding claim, wherein said phosphate is
added to the sol before mixing with the grog.

15

16 A method as claimed in any of claims 1-14, wherein said phosphate is
added in powder form to the refractory material, prior to mixing with the sol.

17 A method as claimed in any preceding claim, wherein said phosphate
20 comprises 0.25%-3%wt monosodium phosphate and/or monopotassium phosphate,
based on the weight of aggregate.

18 A method as claimed in any preceding claim, wherein said silica sol binder
having a pH in the range 10.1-10.6 is provided by adding to a silica sol, having
a pH lower than 10.1, a basic reagent selected from ammonium hydroxide,
potassium hydroxide, sodium hydroxide, sodium silicate, sodium aluminate and
5 potassium silicate.

19 A method for making a refractory object, comprising the steps of binding
a refractory aggregate into a green shape in accordance with the method of any
of claims 1-18, and drying or firing said green shape to form a hardened refractory
10 object.

20 A method as claimed in claim 19, wherein said aggregate is selected from
one or more of zircon, zirconia mullite, alumina, alumina silicates, spinel, silicon
carbide and silica

15

21 A refractory object produced in accordance with the method of claim 19
or claim 20.

22 A method of making a cast refractory substantially as hereinbefore
20 described in the Examples.



Application No: GB 9923941.0
Claims searched: 1 to 22

Examiner: Miss M M Kelman
Date of search: 6 January 2000

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.R): C1J JPA JRB

Int Cl (Ed.7): C04B 35/63

Other: ONLINE:EPODOC, JAPIO, WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
A	EP 0824092 A1 SHAW	
A	US 4769074 A ZYP COATINGS	

X Document indicating lack of novelty or inventive step
Y Document indicating lack of inventive step if combined with one or more other documents of same category.

& Member of the same patent family

A Document indicating technological background and/or state of the art.
P Document published on or after the declared priority date but before the filing date of this invention.
E Patent document published on or after, but with priority date earlier than, the filing date of this application.